Scanning Tunneling Microscopy Study of Spin Properties and Manipulation of Bis(phthalocyaninato) Cerium (CePc2) and Protonated Bis(porphyrinato) Terbium (Tb(Hoep)(oep))

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論　文　内　容　要　旨

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Molecular spintronics have raised a lot of interest that combines spintronics and molecular electronics. The spin coherence length in the organic material is longer than that in the inorganic materials due to the weak spin–orbit coupling and hyperfine interactions, which makes the organic molecules suitable for a spin transport material. Moreover, by combining with photochromism and electrochromism, spin switching should be possible since there is a strong correlation between the structure and electronic properties of molecules. Single-molecule magnets (SMMs) have attracted much attention. SMMs represent a class of compounds in which a single molecule behaves as a magnet. The reported blocking temperature, below which a single SMM molecule works as a quantum magnet, has been increasing with the progress in the molecular design and synthesis techniques of multiple-decker Pc complexes. However, even though the bulk properties of these molecules are promising for the use of electronic materials, the control of the interface between the molecules and the metal-electrode is mandatory for the successful use of these molecules in the spintronic applications. Recently, molecules with magnetic properties adsorbed onto metallic surfaces have been used as platforms to explore the Kondo effect in low dimensions by scanning tunneling microscopy/spectroscopy (STM/STS) such as the family of sandwich-type lanthanide (Ln) complexes with phthalocyaninato (Pc) and porphyrinato (Por) ligands. They have been synthesized, successfully evaporated under a UHV environment and self-assembled on metallic surfaces. Probing 4f-states for late Ln centers with a local probe is difficult since 4f-orbitals are spatially localized around the nucleus and lie deep in energy. Although the Cerium 4f orbital is the most extended in the lanthanide series lying close to the Fermi level, and cerium centers have a mixed-valence promising an original effect, studies on double-decker complexes with cerium centers on surfaces are sparse. Despite their promising properties, Kondo resonance has not been evidenced yet for Ce-based molecular complexes on surfaces.

In the chapter 2, we have explored electric and spin properties of Bis(phthalocyaninato) Cerium ($CePc_2$) for the first time. We deposited $CePc_2$ on Au (111) and found two types of phases. In phase I molecule center is flat and in phase II molecule center contains inner lobes. For the both phases, there are Kondo peak in lobe and center in first layer. In second layer Kondo feature was absent for the both phases. In first layer due to weak interaction with substrate there is charge transfer from ligand to metal and configuration changes from $Ce^{4+}(2Pc^{2-})$ to $Ce^{3+}(Pc^{2-}Pc^{1-})$ consequences spins create in metal and ligand center. X-ray photoelectron spectroscopy shows with increasing thickness of molecule, Ce^{3+} decreases rapidly compared to total (Ce^{3+}+Ce^{4+}) which is good agreement with our dI/dV results.

In the chapter 3, we studied the spin state of the π radical assemblies, which are created through converting nonmagnetic terbium (2,3,7,8,12,13,17,18-octaethy lporphyrinate) (2,3,7,8,12,13,17,18-octaethylporphyrindiate) (Tb(Hoep) (oep)) selectively either into [Tb(oep)$_2$] or deethyl-[Tb(oep)$_2$] radical molecule by removing the H atom and further ethyl group, with the injection of tunneling electrons using a scanning tunneling microscope. The Kondo resonance, formed by screening the radical spin by the conduction electron, shows the dip and peak shapes for [Tb(oep)$_2$] or deethyl-[Tb(oep)$_2$], respectively, due to the difference in the coupling between the two oep ligands. When these two types of molecules are created next to each other, the Kondo resonance appears as a mixture of the peak and dip at the interface of the two. This is interpreted as the result of the hybridization of the two different π radical orbitals, suggesting a possible control of the Kondo state by designing the molecular orbitals.

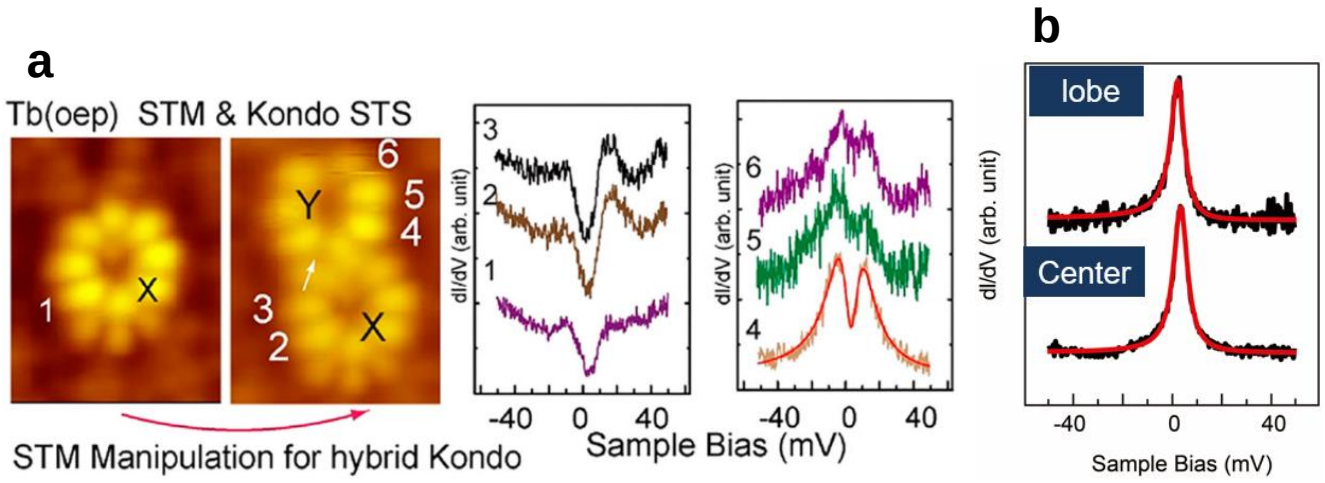

Figure: (a) Molecule X of [Tb(oep)$_2$] obtained after injecting an electron with an energy of 2.0 eV. Molecule Y of deethyl-[Tb(oep)$_2$] created next to X by injecting an electron of 2.5 eV. (c) dI/dV at position 1 of X and 2, 3 of X, and 4–6 on Y. 4 shows mixture of peak & dip.
(b) Kondo resonance on lobe and center in phase I $CePc_2$.

別　紙

論文審査の結果の要旨

本論文は、金基板上におけるセリウムフタロシアニンおよびテルビウムポルフィリンダブルデッカー錯体の電子状態を走査トンネル顕微鏡(STM)および走査トンネル分光(STS)を用いて明らかにし、さらに電流印加により同錯体の電子状態変革について述べている。

第一章では、スピントロニクスと呼ばれる研究分野、単分子磁石と呼ばれる物質系についての紹介、およびスピントロニクスにおける単分子磁石の果たす役割が述べられている。

第二章では、まず、セリウムフタロシアニンダブルデッカー錯体($CePc_2$)を金基板上に真空蒸着するための条件検討を広範に行い、これまで実現されていなかった $CePc_2$ の金基板上への蒸着を初めて実現した。その後、STM を用いることで $Ce(Pc)_2$ の電子状態の解析を行った。蒸着場所により 2 種類の相の存在を確認し、それぞれ Phase I および Phase II とした。STS により電子状態を調べた結果、Phase I, Phase II ともに金基板に直接蒸着された分子では、近藤ピークと呼ばれる電子スピンによる散乱に起因したピークが観測されたのに対し、2 層目では同ピークが観測されなかった。この違いについて、分子層の厚みを変化させ、X 線光電子スペクトル(XPS)を測定したところ、第一層目は Ce の酸化数が+3 であるのに対し、第二層目では Ce の酸化数が+4 であることが示唆された。このように、STS と XPS を相補的に用いることで基板表面に蒸着した $CePc_2$ 分子の酸化状態について詳細に明らかにしている。

第三章では、金基板に蒸着されたテルビウムオクタエチルポルフィリンダブルデッカー錯体($Tb(oep)_2$)について STS を用いてその電子状態を明らかにした。また、電流印加により、ポルフィリン配位子の脱プロトン化、および脱エチル基に成功し、STS と量子化学計算を相補的に用いることで電子状態を明らかにするとともに、電子状態変革に成功している。

第四章では、本論文の総括および今後の研究における課題などについて述べている。

以上の内容は、論文提出者が自立して研究活動を行うために必要な高度の研究能力と学識を有することを示している。したがって、Saiful Islam 提出の博士論文は博士（理学）の学位論文として合格と認める。